ontario hydro
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To: Dr. D. Mills
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A STUDY OF ONTARIO HYDRO'S CONTRIBUTION TO OZONE LEVELS IN ONTARIO
PHASE II - VALIDATION OF A PHOTOCHEMICAL MODULE

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ABSTRACT

This report describes the work done under Phase II of a study of Ontario Hydro's contribution to ozone levels in Ontario. The objective of the current Phase was to validate a comprehensive photochemical module, to be used in a reactive plume model. To do this, a multi-layer box-modelling algorithm was designed based on vertical profile measurements, airborne measurements and the climatology of mixing height. The measurements made during an ozone episode at Dorset, a remote site in central Ontario, during the intensive Canadian Eulerian Model Evaluation Field Study (EMEFS) in the summer of 1988 were used for the evaluation. When measured temperature, NO_x and hydrocarbons, and measurement-calibrated photolysis rates were used as inputs to the model, calculated secondary oxidants showed satisfactory agreement with observations. The module, then, is suitable for our needs and will be employed in the next phase of the study - the development of a reactive plume model for application to Ontario Hydro's emissions.

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1.0 INTRODUCTION

Ozone air quality standards are often exceeded in the Windsor-to-Quebec corridor and authorities are evaluating control options for the precursors NO_x (NO + NO_2) and VOC (volatile organic compounds, also referred to as reactive hydrocarbons). Ozone levels in this part of the country represent the combined effect of medium- to long-range transport of ozone and its precursors as well as local formation due to anthropogenic and natural emissions of NO_x and VOC. Ozone formation depends nonlinearly on precursor concentrations and is influenced by the associated meteorology. The absolute concentrations of NO_x and VOC, as well as their ratio, vary from urban to suburban and rural areas. The relative contribution of natural sources to the atmospheric burden of NO_x and VOC also increases from urban to rural locations. These observations suggest that an effective control strategy needs to recognize the influence of transboundary pollutant transport, the urban vs rural setting as well as the natural vs anthropogenic sources of NO_x and VOC. These aspects are often addressed through the use of photochemical models.

Ontario Hydro is one of the emitters of NO_x in the Province. As such, Hydro is interested in establishing the contribution of its fossil-fuel fired power plants to ozone levels in Ontario. To this end, a study of ozone formation has been initiated. Phase 1 of this study provided a review of the relevant literature, including some of the Eulerian models being used for regional ozone assessment. In the Phase 1 report, the following additional phases were recommended:

- Phase 2 - Design and test a comprehensive photochemical module
- Phase 3 - Develop a reactive plume model
- Phase 4 - Select, modify and apply a Eulerian grid model.

This report describes the work done under Phase 2 of the study of Ontario Hydro's contribution to ozone levels in Ontario.

In the report of Phase I of the Study, it was concluded that a reactive plume model needs to be developed to assess Ontario Hydro's contribution to the ozone burden in Ontario. Before that development can take place, an explicit comprehensive photochemical module, which has been applied to rural areas in both the mid-western and eastern US (Liu et al., 1987; Trainer et al., 1987b and Lin et al., 1988), and is planned for incorporation in the reactive plume model needs to be tested. The measurements made in the Muskoka area of central Ontario during an intensive Canadian Eulerian Model Evaluation Field Study (EMEFS), in the summer of 1988 provide a suitable data base for the evaluation. In the present phase of the Study, an ozone episode observed during EMEFS will be used for this purpose.

In the following sections, the photochemical module will first be described in detail. Then, the measurements taken during the O_3 episode will be presented in Section 3.0 The model design and calculations will be provided and discussed in Section 4.0. Finally, Section 5.0 will provide some concluding remarks.

2.0 PHOTOCHEMICAL MODULE

The photochemical module that will be employed in the development of Ontario Hydro's reactive plume model was originally developed at the US National Oceanic and Atmospheric Administration (NOAA). The module has been used in several studies applied to rural cases in both the mid-western and eastern US (Liu et al., 1987; Trainer et al., 1987b; and Lin et al., 1988).

The photochemical module contains 73 species and 156 reactions as shown in Tables A1 and A2, respectively of Appendix A. In order to overcome the stiffness of the chemical system, a family grouping technique is employed for several short-lived species. These are: a group of O_3, $O(^1D)$, $O(^3P)$ and NO_2; and a group of NO, NO_2, NO_3, HONO, HO_2NO_2 and N_2O_5. The chemical mecha-nism for anthropogenic hydrocarbons shown in Table 2 is actually the one proposed by Atkinson et al. (1982), and Atkinson and Lloyd (1984). Since the photochemistry of isoprene is believed to be better understood than that of monoterpenes, the module uses isoprene as a surrogate to represent natural hydrocarbons. The isoprene reaction scheme proposed by Lloyd et al. (1983) was adopted in the model. The reaction rate constants have been updated according to the Jet Propulsion Laboratory (1985) recommendations.

In addition, a pre-processing code is available for calculating the diurnal variations of the photolysis rates, that are necessary for initiating the photochemical computations. The code includes the effects of Rayleigh and Mie scattering based on the study by Anderson and Meier (1979). NASA (1979) data are used to represent solar intensity at the top of the atmosphere. The absorption cross section values obtained by Calvert and Pitts (1966) and the quantum yield determined by Horowitz and Calvert (1982) are used to derive the photolysis rate of formaldehyde.

3.0 MEASUREMENTS DURING THE OZONE EPISODE

The period of August 2 to August 5, 1988 was chosen for the evaluation. During the 4-day period, central Ontario was at the north-western edge of a stagnant high pressure system. Daily maximum temperatures at the Dorset site were above 33°C. In particular, the daily maximum temperatures reached 36°C on August 2 and 3. The ground level concentrations of hydrocarbons (up to C10) were measured 11 times during the four days. Temperature, O_3 and solar intensity were measured every 5 min while NO_x and formaldehyde were observed every 10 min and 30 min, respectively. These measured hydrocarbon, NO_x, temperature, solar intensity, O_3 and formaldehyde data are presented in Table 1 and Figures 1 through 5.

Table 1. Hydrocarbon Measurements (pptv) at Dorset, Ontario, August 2 Through August 5, 1988.

JULIAN DAY	215	215	215	216	216	217	217	217	217	218	218
TIME	1:20	8:40	15:30	10:00	16:00	0:45	8:00	15:00	23:10	10:00	16:30
C2H6	5112	5923	2852	5630	3341	3192	5821	4248	3834	2088	1771
C2H4	2402	1973	517	815	320	686	1678	468	7384	361	322
C2H2	1128	1014	510	984	426	590	1400	656	669	318	222
C3H8	2372	3063	916	2651	1144	2098	2711	1489	1630	768	538
C3H6	174	435	90	223	68	76	188	128	106	49	46
C3H4	40	49	17	34	55	29	91	-	42	21	23
iC4H10	615	806	210	935	321	541	921	372	311	207	111
nC4H10	1563	2103	570	2857	671	1510	2468	828	809	616	238
1C4H8	89	266	33	94	35	51	128	136	83	48	38
iC4H8	201	487	236	291	257	292	166	232	182	108	117
t2C4H8	40	-	13	-	26	71	29	25	-	40	41
BUTADI	14	39	23	10	-	55	37	13	56	18	6
BUTYNE	-	-	-	-	-	-	-	-	-	-	-
iC5H12	885	1112	321	1355	350	1105	1395	489	500	312	166
nC5H12	470	600	141	631	228	706	779	255	312	193	164
neC5H12	26	40	14	43	39	71	23	31	24	15	8
cC5H10	51	65	15	69	25	77	85	28	34	21	18
1C5H10	30	76	41	55	109	67	23	34	53	34	17
iC5H10	-	305	46	125	70	384	-	-	65	105	76
ISOP	40	2767	1154	2002	1999	137	273	773	110	1129	468
nC6H14	292	238	91	209	194	266	379	106	148	76	146
iC6H14	634	765	456	669	303	971	906	402	395	441	146
cC6H12	52	141	27	80	41	29	144	13	19	42	20
C6H12	-	151	11	19	-	29	-	-	-	-	-
C7H16	-	-	25	139	-	343	-	60	-	73	265
C7H14	-	-	-	-	-	-	-	-	-	-	35
C8H18	-	-	-	-	21	150	-	-	-	171	-
C8H16	-	-	-	-	-	-	-	-	-	-	-
C9	-	-	-	-	-	19	-	-	-	-	-
C10	-	-	-	-	-	-	-	-	-	-	-
C11	-	-	-	-	-	-	-	-	-	-	-
C12	-	-	-	-	-	-	-	-	-	-	-
BENZENE	-	-	135	370	438	438	-	120	-	188	130
TOLUENE	-	-	-	55	159	637	-	13	-	212	1529
oXYLENE	-	-	-	-	-	115	-	-	-	69	-
mpXYL	-	-	-	-	23	253	-	-	-	184	-
EtBENZ	-	-	-	-	23	92	-	-	-	69	-
C3BENZ	-	-	-	-	20	346	-	-	-	122	-
AROM	-	-	-	-	-	164	-	-	-	36	-
TERP	-	-	-	-	-	-	-	-	-	-	-

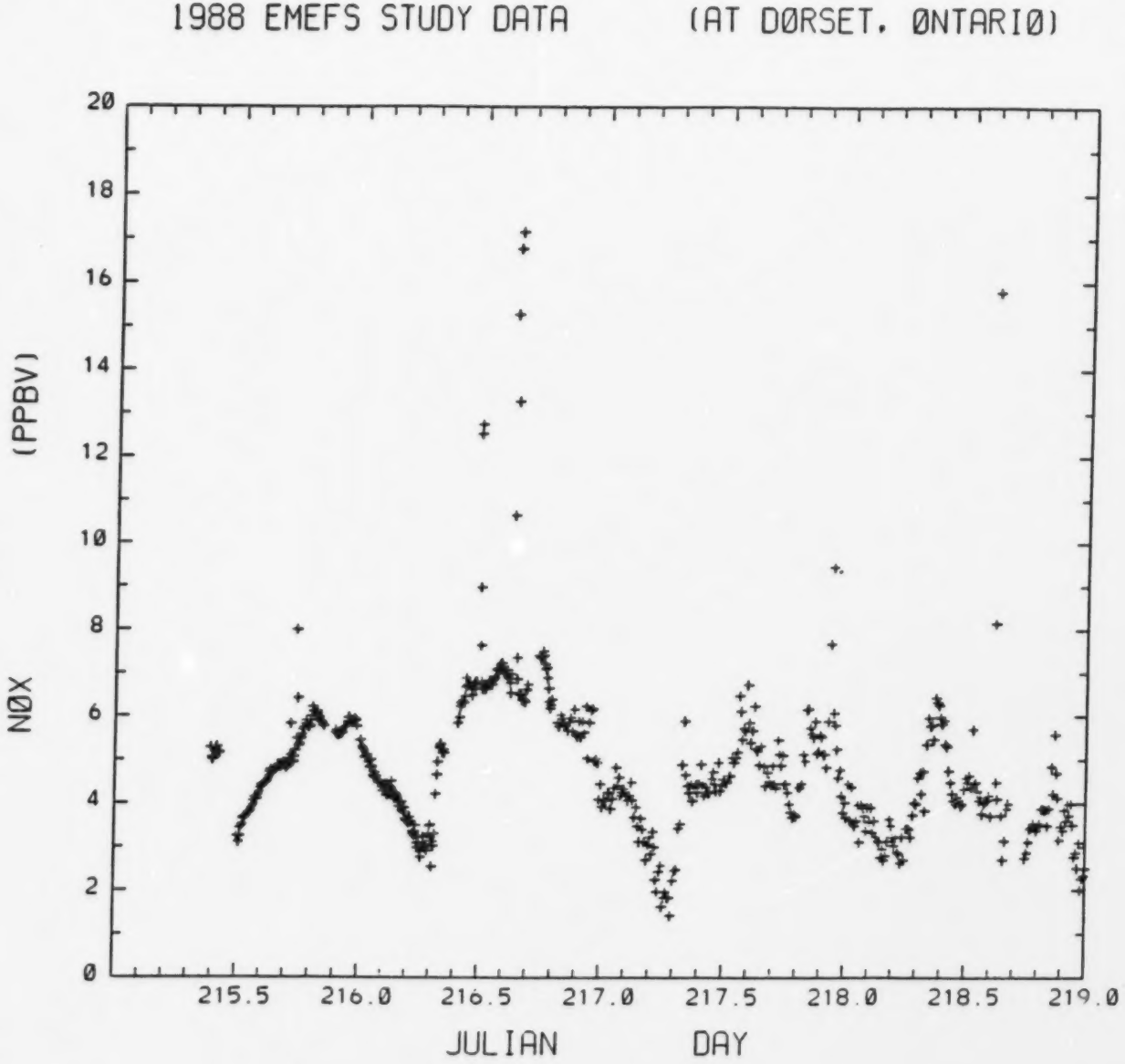

Figure 1. Measured NOx levels at Dorset, Ontario during August 2 to 5, 1988.

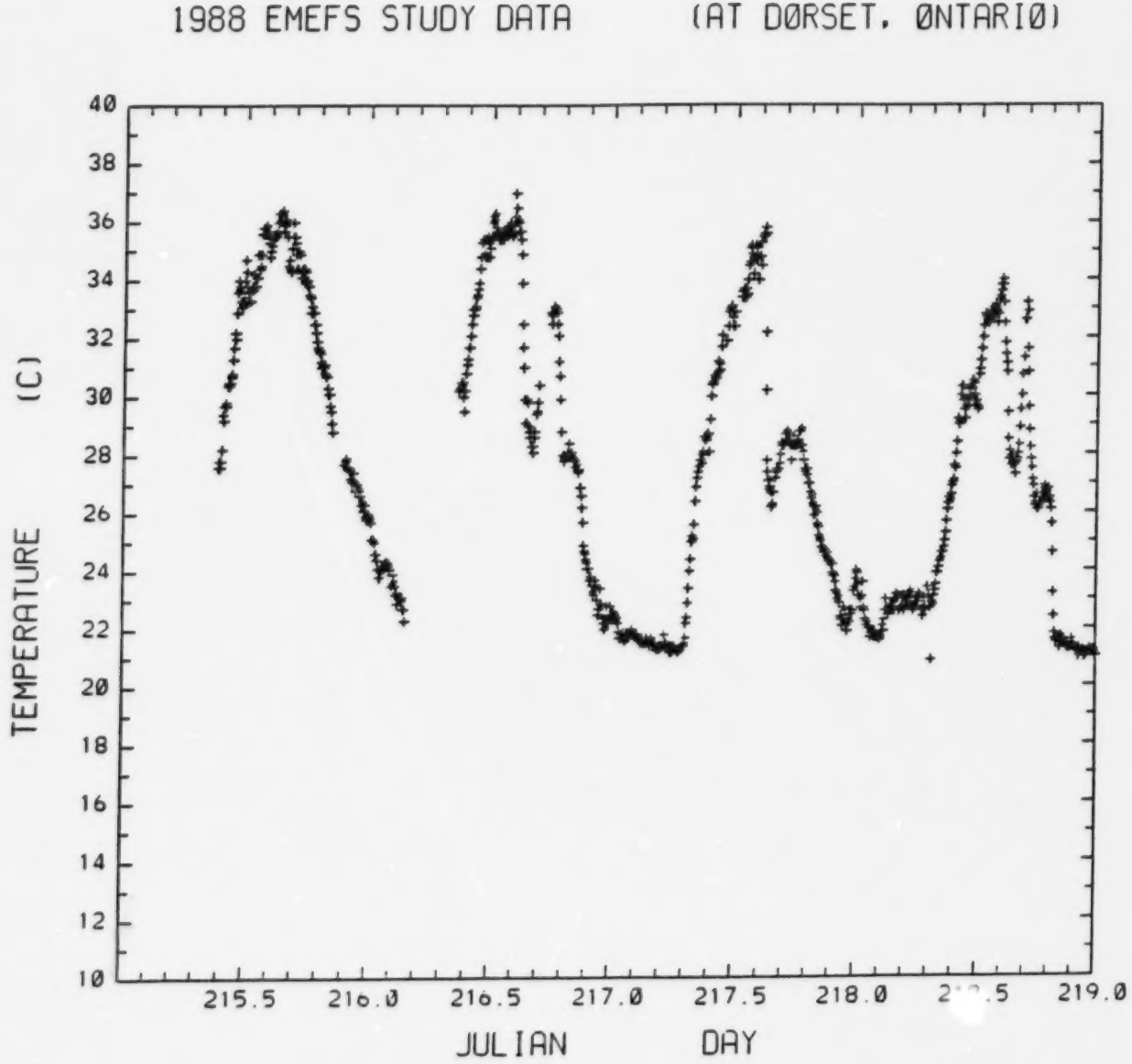

Figure 2. Measured temperature at Dorset, Ontario during August 2 to 5, 1988.

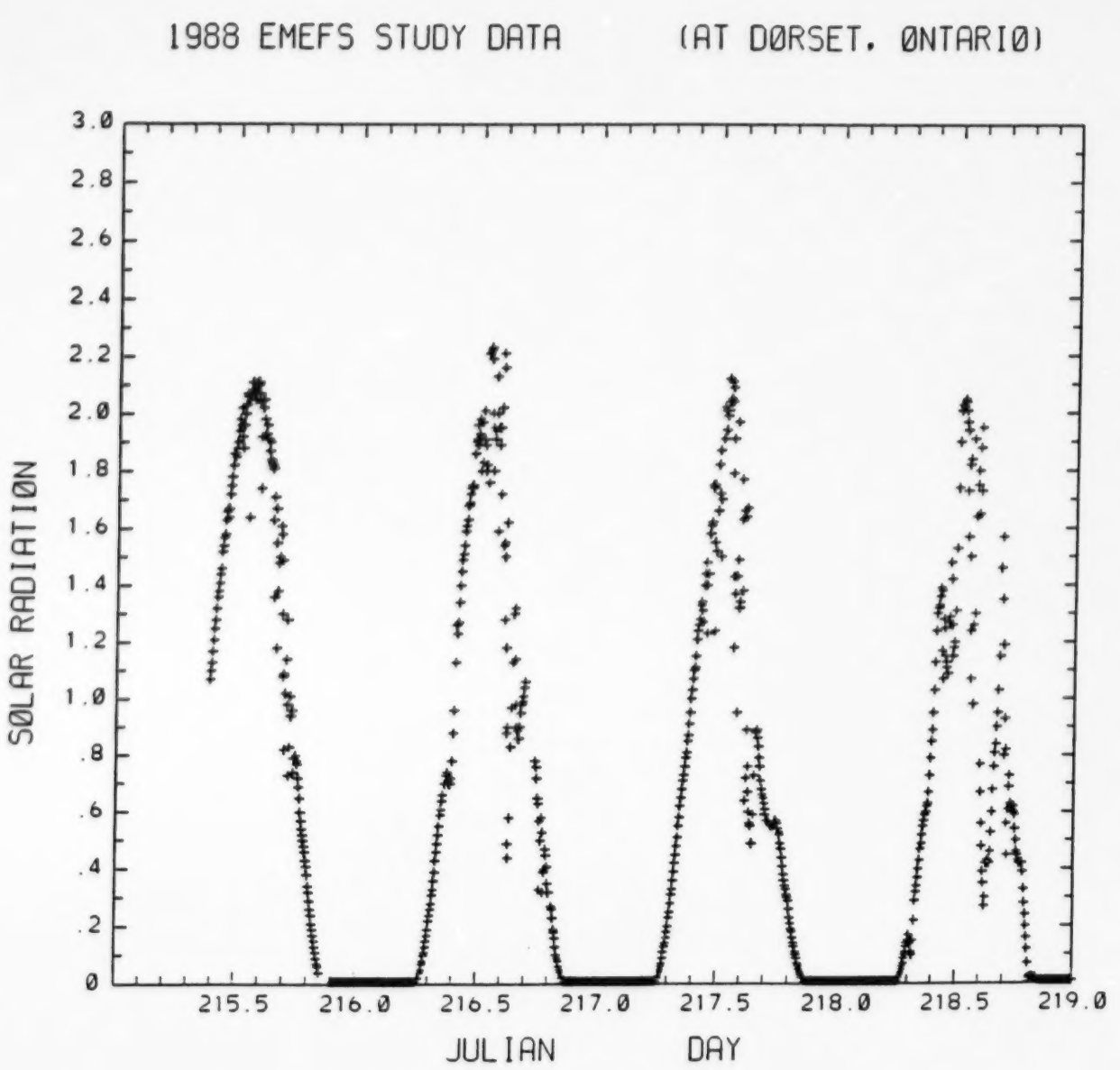

Figure 3. Measured solar intensity at Dorset, Ontario during August 2 to 5, 1988.

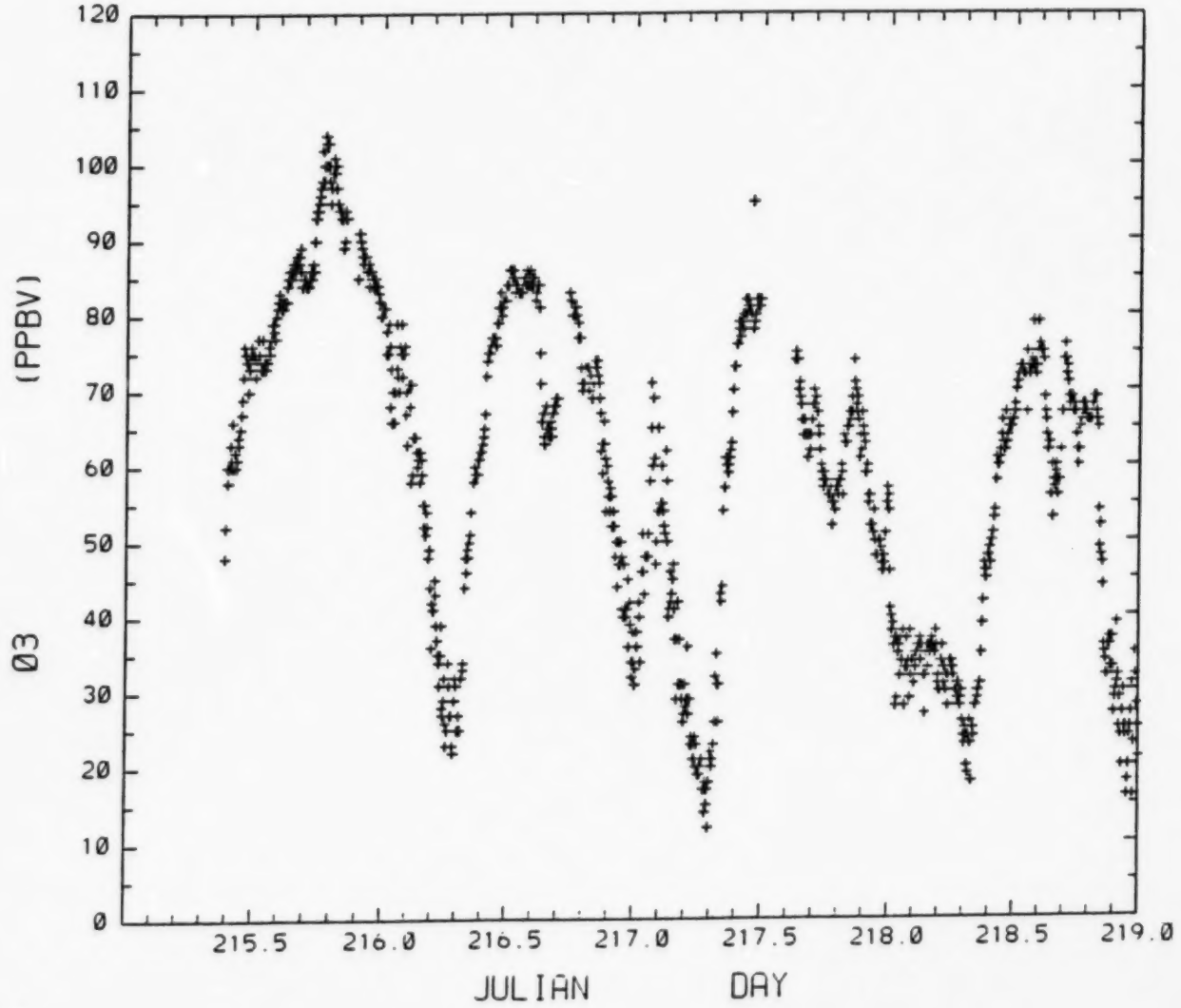

Figure 4. Measured O3 levels at Dorset, Ontario from August 2 to 5 of 1988.

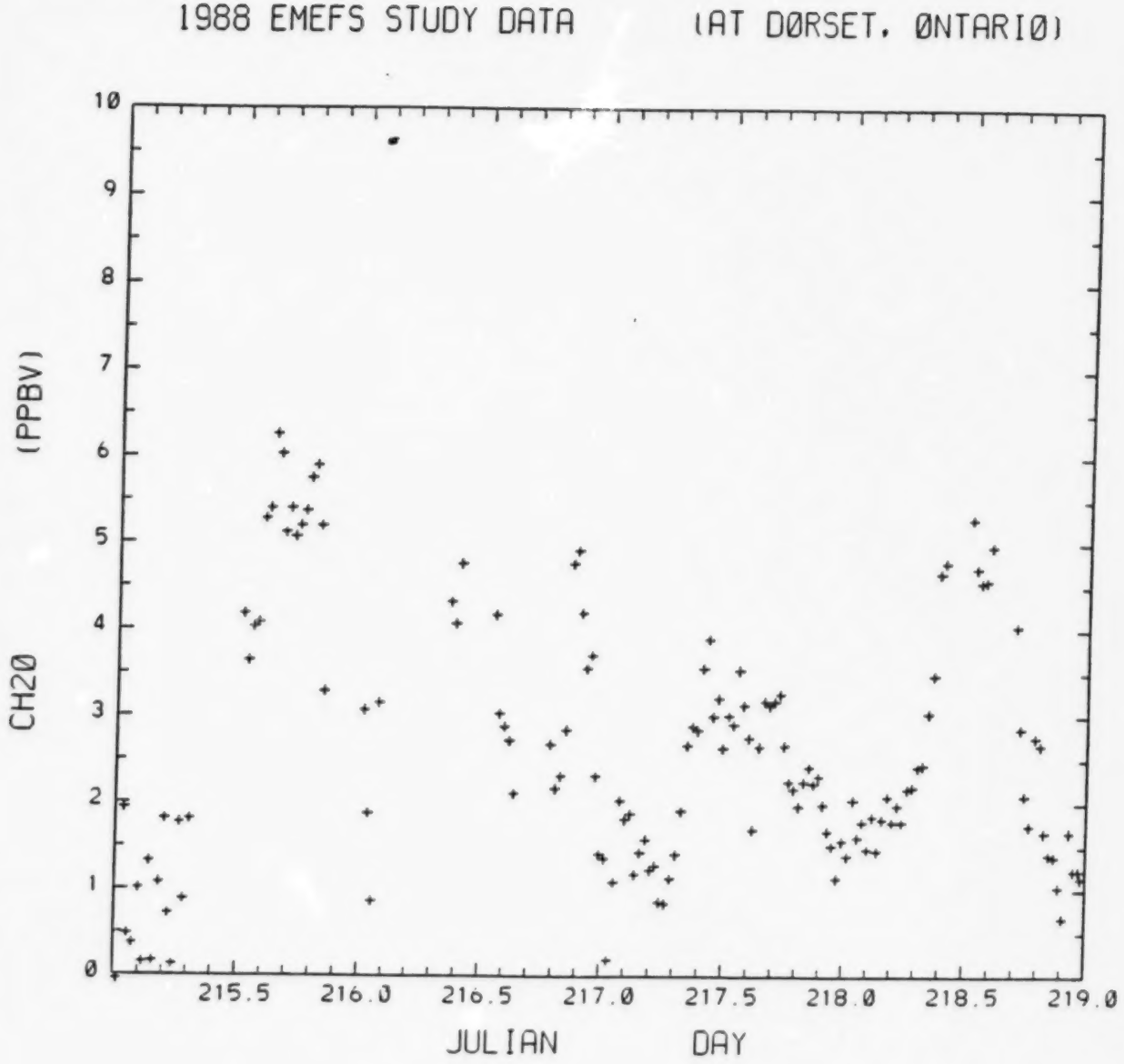

Figure 5. Measured CH2O levels at Dorset, Ontario from August 2 to 5 of 1988.

In the rural troposphere, natural hydrocarbons play an important role in the local production of O_3 since they are highly reactive in reactions involving the hydroxyl radical. On the other hand, the high reactivities result in short lifetimes. For example, in the daytime, the chemical lifetime of isoprene can be as short as half an hour, that is shorter than or comparable to the vertical diffusion time in the planetary boundary layer (PBL). Natural hydrocarbons are emitted into the chemical system from the underlying vegetation. Such an emission, together with the short lifetime, leads to a rapid fall-off of natural hydrocarbon concentrations with height in the troposphere (Hov et al., 1983; Trainer et al., 1987a). This is quite different from the vertical distributions of trace gases of anthropogenic origin, after transport (advection) from other regions. For the latter, a uniform concentration throughout the PBL can be reasonably assumed, whereas it would be improper to simply use a single uniform box to cover the whole PBL in calculating O_3 and other secondary pollutants in the presence of natural hydrocarbons.

In the present study, the PBL is treated as two layers as will be described in the next section. Concentrations of isoprene, which is used as a surrogate for natural hydrocarbons, were treated differently in the two layers. In the lower layer, isoprene was set to the measured value while the concentration in the upper layer was set to zero. The reasons for doing this lie in the following facts.

- Firstly, due to the specific valley-type topography of the Dorset site, the strong turbulent process in the lower part of the PBL during a sunny summer day mixes isoprene fairly well up to about 150 m. This can be confirmed through a separate field study of vertical isoprene profiles by Ontario Hydro at the Dorset site, at 1 pm on August 1, 1989. The preliminary study measured the isoprene concentrations up to about 300 m at 4 levels using a stationary helium balloon. For this typical strong convective case, concurrent vertical measurements of isoprene and temperature are plotted in Figure 6. It is seen that isoprene was well mixed in the lower PBL whereas its mixing ratio fell off rapidly above about 150 m.

- Secondly, several aircraft measurements were made in the Dorset-Egbert area during the first week of August 1988. Two airborne data sets from the Dorset site indicated that isoprene concentrations were 0.1 ppbv at 420 m above the ground in the afternoon of August 4 while the ground level concentrations were about 0.7 ppbv (Strapp et al., 1989).

4.0 MODEL DESIGN AND CALCULATIONS

The Dorset site is characterized by a shallow nocturnal inversion layer with a depth of about 150 m. The inversion layer separates the air aloft from the surface. Therefore, chemical species in the air above the inversion layer do not experience depletion due to dry deposition whereas those confined in the inversion layer are suppressed by surface loss. After sunrise, breakup of the nocturnal layer results in downward mixing of the air from above the surface layer. The downward mixing is responsible for the observed increases of O_3 and other secondary pollutants in the morning hours. During the daytime, the PBL develops up to 1000 m above the ground (Dr. P. Chen, Atmospheric Environment Service, personal communication 1989) and then is followed by the formation of the radiation inversion around sunset.

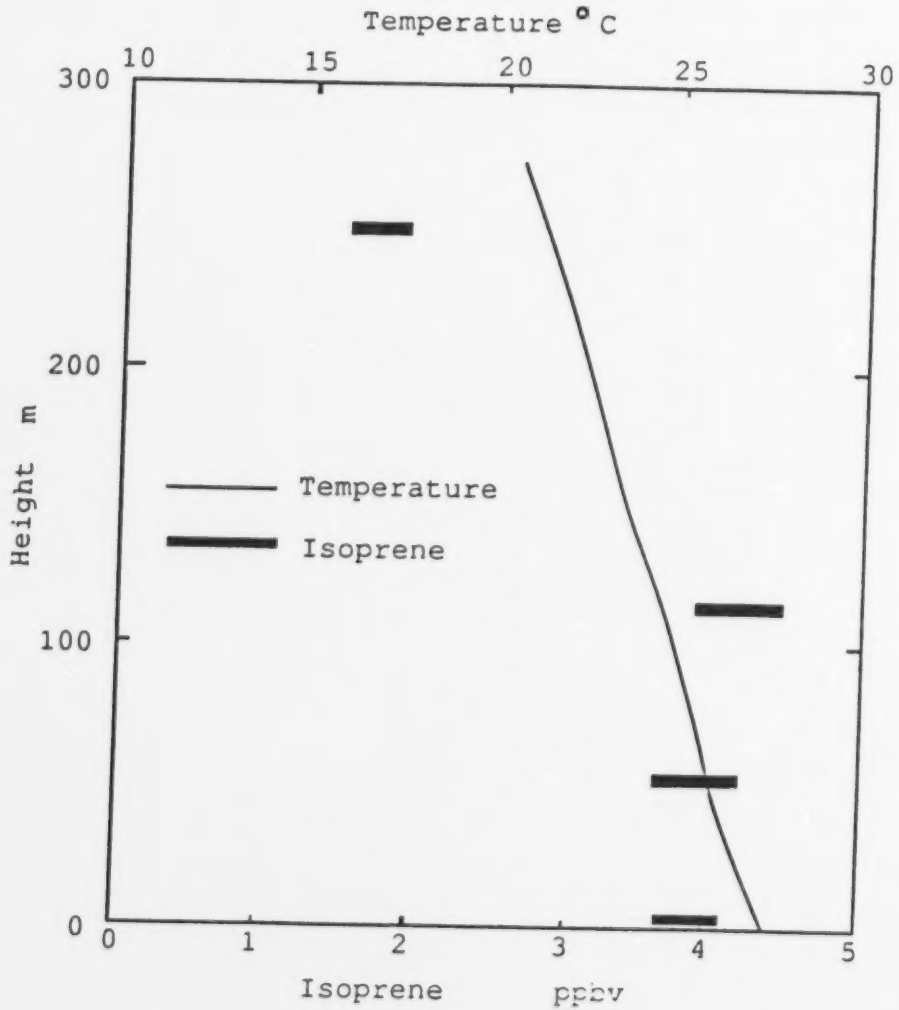

Figure 6. Concurrent measurements of vertical profiles of isoprene and temperature at Dorset, Ontario, at 13:37 on August 1, 1989.

Based on the above considerations, the following box-modelling algorithm was designed. The diurnal variation of mixing height was defined according to the climatology stated above and is presented in Figure 7. During the night, two boxes are applied to the nocturnal inversion layer and the air above, respectively. Calculations of the inversion layer include losses due to deposition to the surface while calculations of the upper box do not. In the following morning, species from the air above and from the air below undergo mixing as the nocturnal inversion breaks up. The mixing rate is determined by the rate of change of the mixing height. During the daytime, two boxes are imposed on the air mass between the surface and 150 m, and the air mass from 150 m up to the mixing height, respectively. The contents of the two air masses are mixed every 40 minutes according to the depths of the two layers. In all cases, the isoprene concentration is set to zero above 150 m while the measured values are used below 150 m for the reasons stated in the previous section.

Before starting the model run, the pre-processing code was used to generate the diurnal variations of photolysis rates for relevant species, for a cloud-free condition at 45 N on August 2 to 5, 1988. These calculated photolysis rates were then calibrated by using the ratio of measured solar intensity to that observed on August 18 1988, a clear sky day. The calibrated photolysis rates, together with measured O_3 precursors, NO_x and hydrocarbons, were used as inputs to the model. Since only a limited number of the measurements were made at discrete times, linear interpolation was employed to extend the data set over the 4-day modelling period.

Dry deposition velocities were specified for the several species which can be significantly removed from the atmosphere by surface deposition. For O_3, dry deposition is a major loss mechanism during the night. In the study, a value of 0.5 cm/s for O_3 was used. This value is within the range given by Aldaz (1969), Galbally and Roy (1980), Wesely et al. (1981), Lenschow et al. (1982) and Colbeck and Harrison (1985). A deposition velocity of 1 cm/s was adopted for HNO_3 from Huebert and Robert (1985). Because of lack of information, the deposition velocities for several other secondary products were arbitrarily set as follows: 0.5 cm/s for H_2O_2 and CH_3OOH, and 0.75 cm/s for aldehydes.

Background levels of CO and CH_4 were assumed to be 200 ppbv and 1600 ppbv, respectively. The model was started for a 4-day initial run (warm-up period). The calibrated photolysis rates, the observed diurnal variations of temperature, NO_x and hydrocarbons of August 2, 1988 were used as inputs for the 4-day period. To do this, we simply re-defined these input variables as the preset values at corresponding times after each step of integration. After the 4 days of simulation, steady diurnal variations of chemical species were established. The variations of the input variables were then released to the actual variations from August 3 to August 5, 1988. Modelled results from the 4th model day to the 7th were extracted and were compared with measurements made during the O_3 episode.

Calculated O_3 concentrations are plotted against time for the 4-day episode in Figure 8. For comparison, the corresponding observed O_3 variation shown in Figure 4 is reproduced in Figure 8. It is apparent that the model calculation reproduced the main features of the observed O_3 episode well. These are, the general diurnal pattern and the peak concentrations, which ranged from 75 to 105 ppbv, with the highest values at the start of the episode. A similar comparison for formaldehyde is presented in Figure 9. It is seen that the model did not

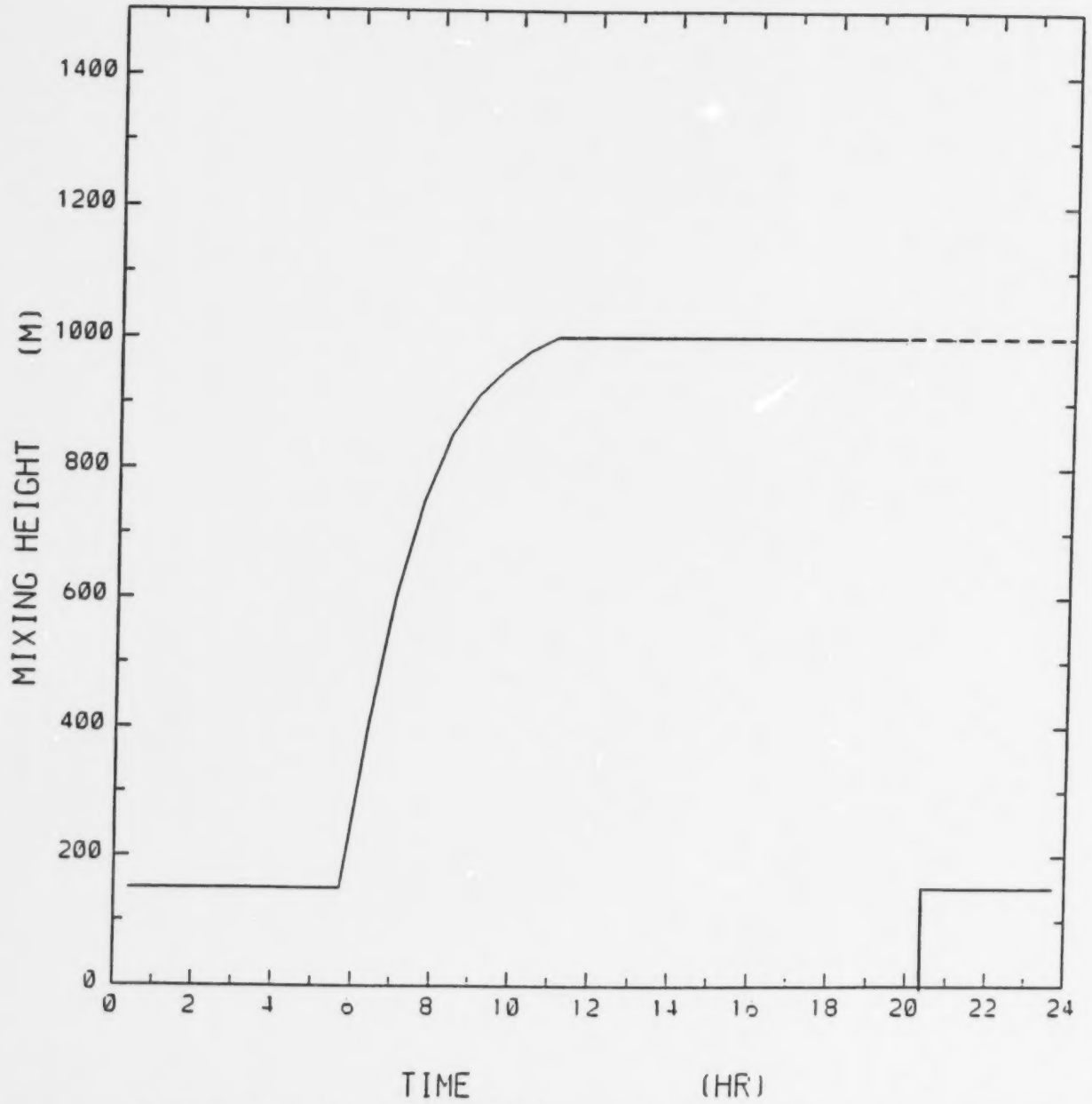

Figure 7. Diurnal variation of mixing height at Dorset, Ontario for the summer

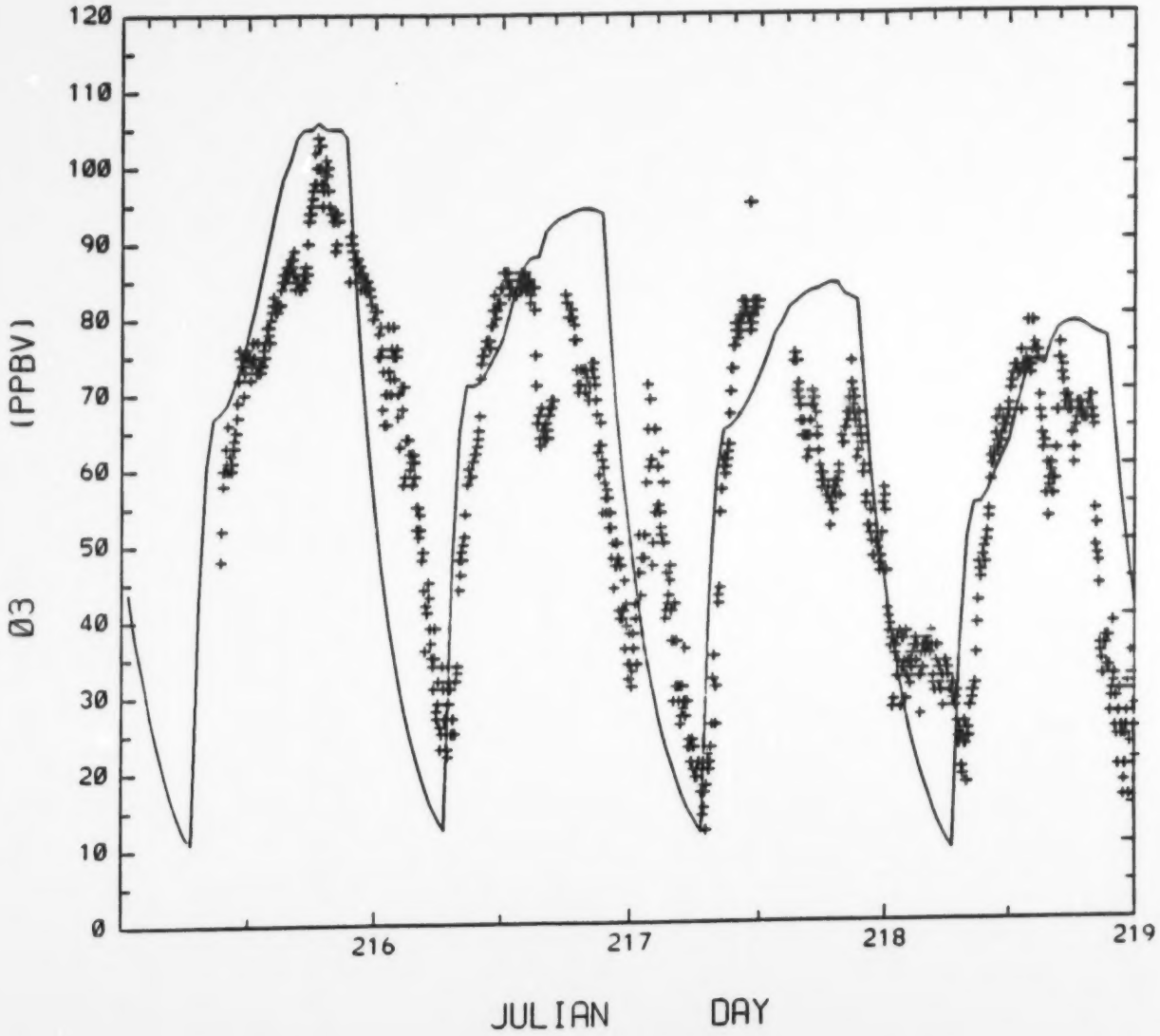

Figure 8. Calculated O3 variation at Dorset, Ontario for August 2 to 5, 1988 is compared with the measurements.

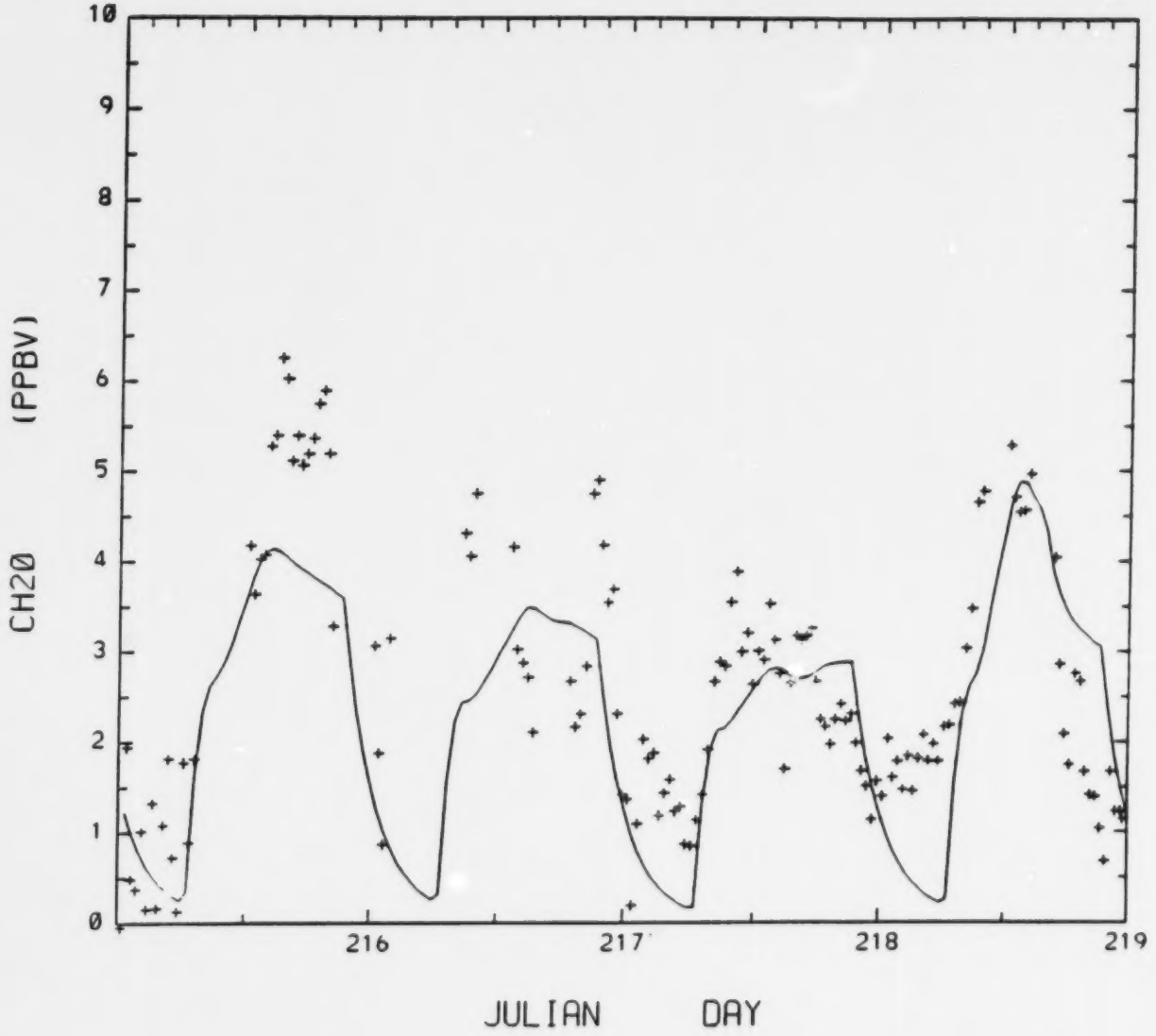

Figure 9. Calculated CH2O variation at Dorset, Ontario for August 2 to 5, 1988 is compared with the measurements.

predict the variation of formaldehyde as well as the variation of O_3. During the first two days, differences between the predicted and the observed formaldehyde variations reach as high as 50%. This might be partially attributable to the treatment of photochemistry; hydrocarbons with carbon number larger than 4 were substituted by butane. Considering the short lifetime of formaldehyde (hours during the daytime), we can reasonably conclude that the results from the current model calculation show satisfactory agreement with the observed O_3 episode.

5.0 CONCLUSIONS

In the present report, the intensive measurements made during a stagnant O_3 episode at the Dorset site in central Ontario during August 2 to 5, 1988 were used to test a photochemical module. By using a multi-layer box treatment with the following inputs

- measurement-calibrated photolysis rates,
- measured temperature,
- measured NO_x, and
- measured hydrocarbons

supported by vertical profile data, airborne data and the PBL climatology, the module successfully reproduced the O_3 variation during the episode. This demonstrates that the module is capable of describing the highly nonlinear relationship between O_3 and its precursors, NO_x and hydrocarbons. Therefore, the chemical module will be used in the next phase of this project - the development of a reactive plume model for use at Ontario Hydro.

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APPENDIX A

Table A1. Chemical Species Included in the Photochemical Module.

	NAME	COMMENT
1	O3	
2	O(1D)	
3	CH4	Methane
4	CO	
5	H2	
6	CO2	
7	H2O	Water Vapor
8	N2	
9	O2	
10	CH3OH	Methanol
11	PRODUCTS	STABLE OR UNKNOWN PRODUCTS
12	NO	
13	NO2	
14	HNO3	Nitric Acid
15	H2O2	Hydrogen Peroxide
16	CH3OOH	Hydrogen Methyl Peroxide
17	CH2O	Formaldehyde
18	CH3CHO	Acetaldehyde
19	PAN	Peroxyacetylnitrate, $CH_3COO_2NO_2$
20	C2H6	Ethane
21	C3H8	Propane
22	C4H10	Butane
23	C2H4	Ethene
24	C3H6	Propene
25	PPN	Peroxypropionylnitrate, $CH_3CH_2COO_2NO_2$
26	MEK	Methylethylketone, $CH_3COCH_2CH_3$
27	RCHO	Propionaldehyde, CH_3CH_2CHO
28	ISOPRENE	$CH_2CHC(CH_3)CH_2$
29	MVK	Methylvinylketone, $CH_3COCHCH_2$
30	MACR	Methacrolein, $CH_2C(CH_3)CHO$
31	HAC	Hydroxyacetaldehyde, $HOCH_2CHO$
32	MGLYX	Methylglyoxal
33	HPAN	$HOCH_2COO_2NO_2$ (FROM HAC)
34	MPAN	$CH_2C(CH_3)COO_2NO_2$ (FROM MACR)
35	HCOOH	Formic Acid
36	CH3COOH	Acetic Acid
37	ORGNIT	Organic Nitrates
38	SO2	
39	SO4	
40	TOLUENE	$C_6H_5CH_3$
41	CRESOL	$HOC_6H_4CH_3$
42	GLYX	Glyoxal
43	DICARB	Dicarbonyl, e.g. $CH_3COCHCHCHO$
44	EPAN	FROM DICARB; e.g. $CH_3COCHCHCOO_2NO_2$
45	OH	

Table 1. (Continued)

	NAME	COMMENT
46	HO2	
47	NO3	
48	N2O5	
49	HONO	Nitrous Acid
50	CH3O2	Methylperoxy Radical
51	CH3COO2	Peroxyacetyl Radical
52	HO2NO2	Peroxynitricacid
53	C2H5O2	Ethylperoxy Radical
54	C3H7O2	Propylperoxy Radical, $CH_3CH(OO)CH_3$
55	C4H9O2	Butylperoxy Radical, $CH_3CH(OO)CH_2CH_3$
56	ETHEO2	Hydroxyethylperoxy Radical, $HOCH_2CH_2O_2$
57	PROPEO2	Hydroxypropylperoxy Radical, $HOCH_2CHO_2CH_3$
58	RCOO2	Peroxypropionyl Radical, $CH_3CH_2COO_2$
59	MEKO2	MEK-RO_2, $C_2H_4O_2COCH_3$
60	RO2	Sum of Peroxyradicals (not HO_2)
61	CH2OO	Criegee
62	CH3CHOO	Criegee
63	RJSOO2	Isoprene-RO_2
64	MVKOO	MVK Criegee
65	MAOO	MACR Criegee
66	MVKO2	MVK-RO_2
67	HAC02	HAC-RO_2, $HOCH_2COO_2$
68	MAO3	MACR-RO_2, $CH_2C(CH_3)COO_2$
69	MRO2	MACR-RO_2, $HOCHCO_2(CH_3)CHO$
70	MCRIG	$CH_3COCHOO$ Criegee
71	ADDO2	Toluene-RO_2
72	CRO2	Cresol-RO_2
73	ERO2	Dicarbonyl-RO_2; e.g. $CH_3COCHCHCOO_2$

Table A2. Reaction Scheme of the Photochemical Module.

1	$O1D + (N_2 + O_2) \rightarrow O_3$
2	$O1D + H_2O \rightarrow 2OH$
3	$O1D + CH_4 \rightarrow .91CH_3O_2 + .91OH + .09CH_2O$
4	$OH + CH_4 \rightarrow CH_3O_2 + H_2O$
5	$O1D + H_2 \rightarrow HO_2 + OH$
6	$OH + H_2 \rightarrow HO_2 + H_2O$
7	$OH + CO \rightarrow HO_2 + CO_2$
8	$OH + HO_2 \rightarrow H_2O + O_2$
9	$OH + O_3 \rightarrow HO_2 + O_2$
10	$HO_2 + O_3 \rightarrow OH + 2O_2$
11	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
12	$OH + H_2O_2 \rightarrow HO_2 + H_2O$
13	$HO_2 + NO \rightarrow OH + NO_2$
14	$NO + O_3 \rightarrow NO_2 + O_2$
15	$OH + HNO_3 \rightarrow H_2O + NO_3$
16	$OH + NO_2 \rightarrow HNO_3$
17	$NO + NO_3 \rightarrow 2NO_2$
18	$NO_2 + O_3 \rightarrow NO_3 + O_2$
19	$NO_2 + NO_3 \rightarrow N_2O_5$
20	$N_2O_5 \rightarrow NO_2 + NO_3$
21	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$
22	$HO_2 + NO_3 \rightarrow .6OH + .6NO_2 + .4HNO_3$
23	$CH_2O + NO_3 \rightarrow HO_2 + HNO_3 + CO$
24	$ISOPRENE + NO_3 \rightarrow ORGNIT$

Table 2. (Continued)

25	$C_3H_6 + NO_3 \rightarrow ORGNIT$
26	$CH_3CHO + NO_3 \rightarrow CH_3COO_2 + HNO_3$
27	$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$
28	$CH_3O_2 + CH_3O_2 \rightarrow .38(2HO_2+2CH_2O) + .62CH_2O + (.62CH_3OH)$
29	$OH + CH_3OOH \rightarrow .56(CH_3O_2+H_2O) + .44(CH_2O+OH+H_2O)$
30	$CH_3O_2 + NO \rightarrow HO_2 + CH_2O + NO_2$
31	$OH + CH_2O \rightarrow HO_2 + H_2O + CO$
32	$OH + NO \rightarrow HONO$
33	$NO + NO_2 + H_2O \rightarrow 2HONO$
34	$N_2O_5 + H_2O \rightarrow 2HNO_3$ (->HOMOGENEOUS ALMOST ZERO)
35	$HO_2 + NO_2 \rightarrow HO_2NO_2$
36	$HO_2NO_2 + OH \rightarrow NO_2 +$ PRODUCTS
37	$HO_2NO_2 \rightarrow HO_2 + NO_2$
38	$OH + SO_2 \rightarrow HO_2 + SO_4$
39	$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$
40	$CH_3COO_2 + CH_3O_2 \rightarrow HO_2 + CH_3O_2 + CH_2O$
41	$CH_3COO_2 + CH_3COO_2 \rightarrow 2CH_3O_2 + 2CO_2$
42	$OH + PAN \rightarrow CH_2O + ?$
43	$OH + CH_3CHO \rightarrow CH_3COO_2 + H_2O$
44	$CH_3COO_2 + NO_2 \rightarrow PAN$
45	$PAN \rightarrow CH_3COO_2 + NO_2$
46	$CH_3COO_2 + NO \rightarrow CH_3O_2 + NO_2 + CO_2$
47	$OH + C_2H_6 \rightarrow C_2H_5O_2 + H_2O$

Table 2. (Continued)

48	$NO + C_2H_5O_2 \rightarrow CH_3CHO + NO_2 + HO_2$
49	$OH + C_3H_8 \rightarrow C_3H_7O_2 + H_2O$
50	$C_3H_7O_2 + NO \rightarrow .31RCHO + NO_2 + HO_2$
51	$OH + C_4H_10 \rightarrow C_4H_9O_2 + H_2O$
52	$NO+C_4H_9O_2 \rightarrow .9NO_2 + .6HO_2 + .29(C_2H_5O_2 + CH_3CHO) + .47MEK + .129RCHO + .1ORGNIT$
53	$OH + C_2H_4 \rightarrow ETHEO_2$
54	$NO + ETHEO_2 \rightarrow 2CH_2O + NO_2 + HO_2$
55	$OH + C_3H_6 \rightarrow PROPEO_2$
56	$NO + PROPEO_2 \rightarrow CH_2O + CH_3CHO + NO_2 + HO_2$
57	$C_2H_4 + O_3 \rightarrow CH_2O + .4CH_2OO + .42CO + .12HO_2 (+.12H_2+.18CO_2+.42H_2O)$
58	$C_3H_6+O_3 \rightarrow .525CH_2O + .5CH_3CHO + .2CH_2OO + .2CH_3CHOO + .095OH + .23HO_2+.215CH_3O_2+.33CO (+.06CH_4+.06H_2+.27CO_2+.21H_2O)$
59	$NO + CH_2OO \rightarrow NO_2 + CH_2O$
60	$NO_2 + CH_2OO \rightarrow NO_3 + CH_2O$
61	$CH_2OO + SO_2 \rightarrow CH_2O + SO_4$
62	$CH_2O + CH_2OO \rightarrow ?$
63	$H_2O + CH_2OO \rightarrow HCOOH$
64	$CH_3CHOO + NO \rightarrow NO_2 + CH_3CHO$
65	$CH_3CHOO + NO_2 \rightarrow NO_3 + CH_3CHO$
66	$CH_3CHOO + SO_2 \rightarrow CH_3CHO + SO_4$
67	$CH_3CHOO + CH_2O \rightarrow ?$
68	$CH_3CHOO + H_2O \rightarrow CH_3COOH$
69	$HO_2 + CH_3COO_2 \rightarrow .75CH_3OOH + .25O_3 + .25CH_3COOH$

Tabe 2. (Continued)

70	$HO_2 + C_2H_3O_2 \rightarrow CH_3OOH$
71	$HO_2 + C_3H_7O_2 \rightarrow CH_3OOH$
72	HO2 + C4H9O2 -> CH_3OOH
73	$HO_2 + ETHEO_2 \rightarrow CH_3OOH$
74	$HO_2 + PROPEO_2 \rightarrow CH_3OOH$
75	$HO_2 + RCOO_2 \rightarrow CH_3OOH$
76	$HO_2 + MEKO_2 \rightarrow CH_3OOH$
77	$HO_2 + RJSOO_2 \rightarrow CH_3OOH$
78	$HO_2 + MVKO_2 \rightarrow CH_3OOH$
79	$HO_2 + HACO_2 \rightarrow CH_3OOH$
80	$HO_2 + MAO_3 \rightarrow CH_3OOH$
81	$HO_2 + MRO_2 \rightarrow CH_3OOH$
82	$HO_2 + ADDO_2 \rightarrow CH_3OOH$
83	$HO_2 + CRO_2 \rightarrow CH_3OOH$
84	$HO_2 + ERO_2 \rightarrow CH_3OOH$
85	$OH + RCHO \rightarrow RCOO_2 + H_2O$
86	$NO_2 + RCOO_2 \rightarrow PPN$
87	$PPN \rightarrow NO_2 + RCOO_2$
88	$NO + RCOO_2 \rightarrow C_2H_3O_2 + NO_2 + CO_2$
89	$OH + MEK \rightarrow MEKO_2 + H_2O$
90	$NO + MEKO_2 \rightarrow NO_2 + CH_3CHO + CH_3COO_2$
91	$OH + TOLUENE \rightarrow .16HO_2 + .84ADDO_2 + .16CRESOL$
92	$NO + ADDO_2 \rightarrow HO_2 + NO_2 + .9DICARB + .72MGLYX + .18GLYX$

Table 2. (Continued)

93	$OH + DICARB \rightarrow ERO_2$
94	$ERO_2 + NO_2 \rightarrow EPAN$
95	$EPAN \rightarrow ERO_2 + NO_2$
96	$ERO_2 + NO \rightarrow -2NO + HO_2 + 3NO_2 + CO + GLYX$
97	$OH + GLYX \rightarrow HO_2 + 2CO$
98	$OH + MGLYX \rightarrow CH_3COO_2 + CO + H_2O$
99	$OH + ISOPRENE \rightarrow RJSOO_2$
100	$NO+RJSOO_2 \rightarrow .9(NO_2+HO_2+CH_2O)+.45(MVK+MACR)+.1ORGNIT$
101	$O_3+ISOPRENE \rightarrow .2(MVK+CH_2OO+MVKOO)+.3(MACR+MAOO)+.5CH_2O+.06HO_2$
102	$NO + MVKOO \rightarrow MVK + NO_2$
103	$NO_2 + MVKOO \rightarrow MVK + NO_3$
104	$H_2O + MVKOO \rightarrow$ STABLE PRODUCT
105	$NO + MAOO \rightarrow MACR + NO_2$
106	$NO_2 + MAOO \rightarrow MACR + NO_3$
107	$H_2O + MAOO \rightarrow$ STABLE PRODUCT
108	$OH + MVK \rightarrow MVKO_2$
109	$NO+MVKO_2 \rightarrow .315(MGLYX+HO_2+CH_2O)+.585(CH_3COO_2+HAC)+.9NO_2+.1ORGNIT$
110	$OH + HAC \rightarrow HACO_2$
111	$NO_2 + HACO_2 \rightarrow HPAN$
112	$HPAN \rightarrow NO_2 + HACO_2$
113	$NO + HACO_2 \rightarrow HO_2 + CH_2O + NO_2$
114	$OH + MACR \rightarrow MAO_3$
115	$NO + MAO_3 \rightarrow -2NO + 3NO_2 + HO_2 + MGLYX$

Table 2. (Continued)

116	NO_2 +MAO_3 -> MPAN
117	MPAN -> NO_2 + MAO_3
118	OH + MACR -> MRO_2
119	NO + MRO_2 -> .9(NO_2 + HO_2 + CH_2O + MGLYX) + .1ORGNIT
120	O_3+MVK->.5(CH_2O+MGLYX)+.2(CH_2OO+HO_2+MCRIG)+.15(CH_3CHO+CH_3COO_2)+?
121	O_3+MACR->.5(CH_2O+MGLYX)+.2(CH_2OO+MCRIG)+.21HO_2+.15CH_3O_2+STABLE
122	NO + MCRIG -> MGLYX + NO_2
123	NO_2 + MCRIG -> MGLYX + NO_3
124	H_2O + MCRIG -> STABLE PRODUCTS
125	HCOOH + OH -> HO_2
126	OH + CRESOL -> CRO_2
127	CRO_2 + NO -> HO_2 + NO_2 + DICARB
128	NO_3 + CRESOL -> HNO_3 - NO_2 (+NITROCRESOL)
129	O_3 + hν -> O1D + O_2
130	NO_2 + hν -> NO + O_3
131	H_2O_2 + hν -> OH + OH
132	HNO_3 + hν -> OH + NO_2
133	CH_3OOH + hν -> CH_2O + OH + HO_2
134	HONO + hν -> OH + NO
135	NO_3 + hν -> .891NO_2 + .8913 + .109NO
136	N_2O_5 + hν -> NO_2 + NO_3
137	HO_2NO_2 + hν -> HO_2 + NO_2
138	CH_2O + hν -> 2HO_2 + CO

Table 2. (Continued)

139	$CH_2O + h\nu \rightarrow H_2 + CO$
140	$CH_3CHO + h\nu \rightarrow CH_3O_2 + CO + HO_2$
141	$MEK + h\nu \rightarrow CH_3CO_3 + C_2H_5O_2$
142	$RCHO + h\nu \rightarrow C_2H_5O_2 + CO + HO_2$
143	$HAC + h\nu \rightarrow CH_2O + 2HO_2 + CO$
144	$MGLYX + h\nu \rightarrow CH_3COO_2 + HO_2 + CO$
145	$GLYX + h\nu \rightarrow 1.87CO + .13CH_2O$
146	$DICARB + h\nu \rightarrow HO_2 + ERO_2$
147	HNO_3 HETEROGENEOUS LOSS
148	H_2O_2 HETEROGENEOUS LOSS
149	CH_3OOH HETEROGENEOUS LOSS
150	CH_2O HETEROGENEOUS LOSS
151	HCOOH HETEROGENEOUS LOSS
152	CH_3COOH HETEROGENEOUS LOSS
153	SO_2 HETEROGENEOUS LOSS
154	SO_4 HETEROGENEOUS LOSS
155	CRESOL HETEROGENEOUS LOSS
156	N_2O_5 HETEROGENEOUS LOSS